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9.8 The following standards are approved for incorporation by reference by the Director of the Federal Register in accordance with 5 U.S.C. 552(a) and 1 CFR part 51. Copies may also be inspected at EPA's Water Docket, 1200 Pennsylvania Ave. NW., Washington, DC 20460 and at at the National Archives and Records Administration (NARA). For information on the availability of this material at NARA, call 202–741–6030, or go to: *http://www.archives.gov/federal__register/code__of__federal__regulations/ibr__locations.html*.

9.8.1 ASTM International. Available from ASTM International, 100 Barr Harbor Drive, P.O. Box C700, West Conshohocken, PA 19428–2959, or online at *http://www.astm.org*.

9.8.1.1 ASTM D5291–96, Standard Test Methods for Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Petroleum Products and Lubricants, approved April 10, 1996.

9.8.1.2 ASTM D2974–07a, Standard Test Methods for Moisture, Ash, and Organic Matter of Peat and Other Organic Soils, approved March 15, 2007.

[77 FR 29837, May 18, 2012]

## APPENDIX 5 TO SUBPART A OF PART 435—DETERMINATION OF CRUDE OIL CONTAMINATION IN NON-AQUEOUS DRILLING FLUIDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS) (EPA METHOD 1655)

### 1.0 SCOPE AND APPLICATION

1.1 This method determines crude (formation) oil contamination, or other petroleum oil contamination, in non-aqueous drilling fluids (NAFs) by comparing the gas chromatography/mass spectrometry (GC/MS) fingerprint scan and extracted ion scans of the test sample to that of an uncontaminated sample.

1.2 This method can be used for monitoring oil contamination of NAFs or monitoring oil contamination of the base fluid used in the NAF formulations.

1.3 Any modification of this method beyond those expressly permitted shall be considered as a major modification subject to application and approval of alternative test procedures under 40 CFR 136.4 and 136.5.

1.4 The gas chromatography/mass spectrometry portions of this method are restricted to use by, or under the supervision of analysts experienced in the use of GC/MS and in the interpretation of gas chromatograms and extracted ion scans. Each laboratory that uses this method must generate acceptable results using the procedures described in Sections 7, 9.2, and 12 of this appendix.

### 2.0 SUMMARY OF METHOD

2.1 Analysis of NAF for crude oil contamination is a step-wise process. The analyst first performs a qualitative assessment of the presence or absence of crude oil in the sample. If crude oil is detected during this qualitative assessment, the analyst must perform a quantitative analysis of the crude oil concentration.

2.2 A sample of NAF is centrifuged to obtain a solids free supernate.

2.3 The test sample is prepared by removing an aliquot of the solids free supernate, spiking it with internal standard, and analyzing it using GC/MS techniques. The components are separated by the gas chromatograph and detected by the mass spectrometer.

2.4 Qualitative identification of crude oil contamination is performed by comparing the Total Ion Chromatograph (TIC) scans and Extracted Ion Profile (EIP) scans of test sample to that of uncontaminated base fluids, and examining the profiles for chromatographic signatures diagnostic of oil contamination.

2.5 The presence or absence of crude oil contamination observed in the full scan profiles and selected extracted ion profiles determines further sample quantitation and reporting requirements.

2.6 If crude oil is detected in the qualitative analysis, quantitative analysis must be performed by calibrating the GC/MS using a designated NAF spiked with known concentrations of a designated oil.

2.7 Quality is assured through reproducible calibration and testing of GC/MS system and through analysis of quality control samples.

### 3.0 DEFINITIONS

3.1 A NAF is one in which the continuous—phase is a water immiscible fluid such

as an oleaginous material (e.g., mineral oil, enhance mineral oil, paraffinic oil, or synthetic material such as olefins and vegetable esters).

3.2 TIC—Total Ion Chromatograph.

3.3 EIP—Extracted Ion Profile.

3.4 TCB—1,3,5-trichlorobenzene is used as the internal standard in this method.

3.5 SPTM—System Performance Test Mix standards are used to establish retention times and monitor detection levels.

## 4.0 Interferences and Limitations

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or elevated baselines causing misinterpretation of chromatograms.

4.2 All Materials used in the analysis shall be demonstrated to be free from interferences by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

4.3 Glassware shall be cleaned by rinsing with solvent and baking at 400 °C for a minimum of 1 hour.

4.4 Interferences may vary from source to source, depending on the diversity of the samples being tested.

4.5 Variations in and additions of base fluids and/or drilling fluid additives (emulsifiers, dispersants, fluid loss control agents, etc.) might also cause interferences and misinterpretation of chromatograms.

4.6 Difference in light crude oils, medium crude oils, and heavy crude oils will result in different responses and thus different interpretation of scans and calculated percentages.

## 5.0 Safety

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however each chemical shall be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest possible level.

5.2 Unknown samples may contain high concentration of volatile toxic compounds. Sample containers should be opened in a hood and handled with gloves to prevent exposure. In addition, all sample preparation should be conducted in a fume hood to limit the potential exposure to harmful contaminates.

5.3 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDSs) shall be available to all personnel involved in these analyses. Additional references to laboratory safety can be found in References 16.1 through 16.3.

5.4 NAF base fluids may cause skin irritation, protective gloves are recommended while handling these samples.

## 6.0 Apparatus and Materials

NOTE: Brand names, suppliers, and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using apparatus and materials other than those specified here, but demonstration of equivalent performance meeting the requirements of this method is the responsibility of the laboratory.

6.1 Equipment for glassware cleaning.

6.1.1 Laboratory sink with overhead fume hood.

6.1.2 Kiln—Capable of reaching 450 °C within 2 hours and holding 450 °C within ±10 °C, with temperature controller and safety switch (Cress Manufacturing Co., Santa Fe Springs, CA B31H or X31TS or equivalent).

6.2 Equipment for sample preparation.

6.2.1 Laboratory fume hood.

6.2.2 Analytical balance—Capable of weighing 0.1 mg.

6.2.3 Glassware.

6.2.3.1 Disposable pipettes—Pasteur, 150 mm long by 5 mm ID (Fisher Scientific 13–678–6A, or equivalent) baked at 400 °C for a minimum of 1 hour.

6.2.3.2 Glass volumetric pipettes or gas tight syringes—1.0-mL ±1% and 0.5-mL ±1%.

6.2.3.3 Volumetric flasks—Glass, class A, 10-mL, 50-mL and 100-mL.

6.2.3.4—Sample vials—Glass, 1- to 3-mL (baked at 400 °C for a minimum of 1 hour) with PTFE-lined screw or crimp cap.

6.2.3.5 Centrifuge and centrifuge tubes—Centrifuge capable of 10,000 rpm, or better, (International Equipment Co., IEC Centra MP4 or equivalent) and 50-mL centrifuge tubes (Nalgene, Ultratube, Thin Wall 25×89 mm, #3410–2539).

6.3 Gas Chromatograph/Mass Spectrometer (GC/MS):

6.3.1 Gas Chromatograph—An analytical system complete with a temperature-programmable gas chromatograph suitable for split/splitless injection and all required accessories, including syringes, analytical columns, and gases.

6.3.1.1 Column—30 m (or 60 m) × 0.32 mm ID (or 0.25 mm ID) 1 μm film thickness (or 0.25 μm film thickness) silicone-coated fused-silica capillary column (J&W Scientific DB–5 or equivalent).

6.3.2 Mass Spectrometer—Capable of scanning from 35 to 600 amu every 1 sec or less, using 70 volts (nominal) electron energy in the electron impact ionization mode (Hewlett Packard 5970MS or comparable).

6.3.3 GC/MS interface—the interface is a capillary-direct interface from the GC to the MS.

6.3.4—Data system—A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundance versus retention time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EIP). Software must also be available that allows integrating the abundance in any total ion chromatogram (TIC) or EIP between specified retention time or scan-number limits. It is advisable that the most recent version of the EPA/NIST Mass Spectral Library be available.

7.0 REAGENTS AND STANDARDS

7.1 Methylene chloride—Pesticide grade or equivalent. Use when necessary for sample dilution.

7.2 Standards—Prepare from pure individual standard materials or purchase as certified solutions. If compound purity is 96% or greater, the weight may be used without correction to compute the concentration of the standard.

7.2.1 Crude Oil Reference—Obtain a sample of a crude oil with a known API gravity. This oil shall be used in the calibration procedures.

7.2.2 Synthetic Base Fluid—Obtain a sample of clean internal olefin (IO) Lab drilling fluid (as sent from the supplier—has not been circulated downhole). This drilling fluid shall be used in the calibration procedures.

7.2.3 Internal standard—Prepare a 0.01 g/mL solution of 1,3,5-trichlorobenzene (TCB). Dissolve 1.0 g of TCB in methylene chloride and dilute to volume in a 100-mL volumetric flask. Stopper, vortex, and transfer the solution to a 150-mL bottle with PTFE-lined cap. Label appropriately, and store at –5 °C to 20 °C. Mark the level of the meniscus on the bottle to detect solvent loss.

7.2.4 GC/MS system performance test mix (SPTM) standards—The SPTM standards shall contain octane, decane, dodecane, tetradecane, tetradecene, toluene, ethylbenzene, 1,2,4-trimethylbenzene, 1-methylnaphthalene and 1,3-dimethylnaphthalene. These compounds can be purchased individually or obtained as a mixture (*i.e.*, Supelco, Catalog No. 4–7300). Prepare a high concentration of the SPTM standard at 62.5 mg/mL in methylene chloride. Prepare a medium concentration SPTM standard at 1.25 mg/mL by transferring 1.0 mL of the 62.5 mg/mL solution into a 50 mL volumetric flask and diluting to the mark with methylene chloride. Finally, prepare a low concentration SPTM standard at 0.125 mg/mL by transferring 1.0 mL of the 1.25 mg/mL solution into a 10-mL volumetric flask and diluting to the mark with methylene chloride.

7.2.5 Crude oil/drilling fluid calibration standards—Prepare a 4-point crude oil/drilling fluid calibration at concentrations of 0% (no spike—clean drilling fluid), 0.5%, 1.0%, and 2.0% by weight according to the procedures outlined in this appendix using the Reference Crude Oil:

7.2.5.1 Label 4 jars with the following identification: Jar 1—0%Ref-IOLab, Jar 2—0.5%Ref-IOLab, Jar 3—1%Ref-IOLab, and Jar 4—2%Ref-IOLab.

7.2.5.2 Weigh 4, 50-g aliquots of well mixed IO Lab drilling fluid into each of the 4 jars.

7.2.5.3 Add Reference Oil at 0.5%, 1.0%, and 2.0% by weight to jars 2, 3, and 4 respectively. Jar 1 shall not be spiked with Reference Oil in order to retain a ''0%'' oil concentration.

7.2.5.4 Thoroughly mix the contents of each of the 4 jars, using clean glass stirring rods.

7.2.5.5 Transfer (weigh) a 30-g aliquot from Jar 1 to a labeled centrifuge tube. Centrifuge the aliquot for a minimum of 15 min at approximately 15,000 rpm, in order to obtain a solids free supernate. Weigh 0.5 g of the supernate directly into a tared and appropriately labeled GC straight vial. Spike the 0.5-g supernate with 500 µL of the 0.01g/mL 1,3,5-trichlorobenzene internal standard solution (*see* Section 7.2.3 of this appendix), cap with a Teflon lined crimp cap, and vortex for ca. 10 sec.

7.2.5.6 Repeat step 7.2.5.5 except use an aliquot from Jar 2.

7.2.5.7 Repeat step 7.2.5.5 except use an aliquot from Jar 3.

7.2.5.8 Repeat step 7.2.5.5 except use an aliquot from Jar 4.

7.2.5.9 These 4 crude/oil drilling fluid calibration standards are now used for qualitative and quantitative GC/MS analysis.

7.2.6 Precision and recovery standard (mid level crude oil/drilling fluid calibration standard)—Prepare a mid point crude oil/drilling fluid calibration using IO Lab drilling fluid and Reference Oil at a concentration of 1.0% by weight. Prepare this standard according to the procedures outlined in Section 7.2.5.1 through 7.2.5.5 of this appendix, with the exception that only ''Jar 3'' needs to be prepared. Remove and spike with internal standard, as many 0.5-g aliquots as needed to complete the GC/MS analysis (*see* Section 11.6 of this appendix—bracketing authentic samples every 12 hours with precision and recovery standard) and the initial demonstration exercise described in Section 9.2 of this appendix.

7.2.7 Stability of standards

7.2.7.1 When not used, standards shall be stored in the dark, at −5 to −20 °C in screw-capped vials with PTFE-lined lids. Place a mark on the vial at the level of the solution so that solvent loss by evaporation can be

detected. Bring the vial to room temperature prior to use.

7.2.7.2 Solutions used for quantitative purposes shall be analyzed within 48 hours of preparation and on a monthly basis thereafter for signs of degradation. A standard shall remain acceptable if the peak area remains within ±15% of the area obtained in the initial analysis of the standard.

### 8.0 Sample Collection Preservation and Storage

8.1 Collect NAF and base fluid samples in 100- to 200-mL glass bottles with PTFE- or aluminum foil lined caps.

8.2 Samples collected in the field shall be stored refrigerated until time of preparation.

8.3 Sample and extract holding times for this method have not yet been established. However, based on initial experience with the method, samples should be analyzed within seven to ten days of collection and extracts should be analyzed within seven days of preparation.

8.4 After completion of GC/MS analysis, extracts shall be refrigerated at 4 °C until further notification of sample disposal.

### 9.0 Quality Control

9.1 Each laboratory that uses this method is required to operate a formal quality assurance program (Reference 16.4). The minimum requirements of this program shall consist of an initial demonstration of laboratory capability, and ongoing analysis of standards, and blanks as a test of continued performance, analyses of spiked samples to assess accuracy and analysis of duplicates to assess precision. Laboratory performance shall be compared to established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

9.1.1 The analyst shall make an initial demonstration of the ability to generate acceptable accuracy and precision with this method. This ability shall be established as described in Section 9.2 of this appendix.

9.1.2 The analyst is permitted to modify this method to improve separations or lower the cost of measurements, provided all performance requirements are met. Each time a modification is made to the method, the analyst is required to repeat the calibration (Section 10.4 of this appendix) and to repeat the initial demonstration procedure described in Section 9.2 of this appendix.

9.1.3 Analyses of blanks are required to demonstrate freedom from contamination. The procedures and criteria for analysis of a blank are described in Section 9.3 of this appendix.

9.1.4 Analysis of a matrix spike sample is required to demonstrate method accuracy. The procedure and QC criteria for spiking are described in Section 9.4 of this appendix.

9.1.5 Analysis of a duplicate field sample is required to demonstrate method precision. The procedure and QC criteria for duplicates are described in Section 9.5 of this appendix.

9.1.6 Analysis of a sample of the clean NAF(s) (as sent from the supplier—*i.e.*, has not been circulated downhole) used in the drilling operations is required.

9.1.7 The laboratory shall, on an ongoing basis, demonstrate through calibration verification and the analysis of the precision and recovery standard (Section 7.2.6 of this appendix) that the analysis system is in control. These procedures are described in Section 11.6 of this appendix.

9.1.8 The laboratory shall maintain records to define the quality of data that is generated.

9.2 Initial precision and accuracy—The initial precision and recovery test shall be performed using the precision and recovery standard (1% by weight Reference Oil in IO Lab drilling fluid). The laboratory shall generate acceptable precision and recovery by performing the following operations.

9.2.1 Prepare four separate aliquots of the precision and recovery standard using the procedure outlined in Section 7.2.6 of this appendix. Analyze these aliquots using the procedures outlined in Section 11 of this appendix.

9.2.2 Using the results of the set of four analyses, compute the average recovery (X) in weight percent and the standard deviation of the recovery(s) for each sample.

9.2.3 If s and X meet the acceptance criteria of 80% to 110%, system performance is acceptable and analysis of samples may begin. If, however, s exceeds the precision limit or X falls outside the range for accuracy, system performance is unacceptable. In this event, review this method, correct the problem, and repeat the test.

9.2.4 Accuracy and precision—The average percent recovery (P) and the standard deviation of the percent recovery (Sp) Express the accuracy assessment as a percent recovery interval from $P–2S_p$ to $P+2S_p$. For example, if P=90% and $S_p$=10% for four analyses of crude oil in NAF, the accuracy interval is expressed as 70% to 110%. Update the accuracy assessment on a regular basis.

9.3 Blanks—Rinse glassware and centrifuge tubes used in the method with 30 mL of methylene chloride, remove a 0.5-g aliquot of the solvent, spike it with the 500 µL of the internal standard solution (Section 7.2.3 of this appendix) and analyze a 1-µL aliquot of the blank sample using the procedure in Section 11 of this appendix. Compute results per Section 12 of this appendix.

9.4 Matrix spike sample—Prepare a matrix spike sample according to procedure outlined in Section 7.2.6 of this appendix. Analyze the sample and calculate the concentration (% oil) in the drilling fluid and % recovery of oil from the spiked drilling fluid

using the methods described in Sections 11 and 12 of this appendix.

9.5 Duplicates—A duplicate field sample shall be prepared and analyzed according to Section 11. The relative percent difference (RPD) of the calculated concentrations shall be less than 15%.

9.5.1 Analyze each of the duplicates per the procedure in Section 11 of this appendix and compute the results per Section 12 of this appendix.

9.5.2 Calculate the relative percent difference (RPD) between the two results per the following equation:

$$RPD = \frac{|D_1 - D_2|}{[(D_1 + D_2)/2]} \times 100$$

where:

$D_1$ = Concentration of crude oil in the sample; and

$D_2$ = Concentration of crude oil in the duplicate sample.

9.5.3 If the RPD criteria are not met, the analytical system shall be judged to be out of control, and the problem must be immediately identified and corrected, and the sample batch re-analyzed.

9.6 A clean NAF sample shall be prepared and analyzed according to Section 11. Ultimately the oil-equivalent concentration from the TIC or EIP signal measured in the clean NAF sample shall be subtracted from the corresponding authentic field samples in order to calculate the true contaminant concentration (% oil) in the field samples (*see* Section 12).

9.7 The specifications contained in this method can be met if the apparatus used is calibrated properly, and maintained in a calibrated state. The standards used for initial precision and recovery (Section 9.2 of this appendix) and ongoing precision and recovery (Section 11.6 of this appendix) shall be identical, so that the most precise results will be obtained. The GC/MS instrument will provide the most reproducible results if dedicated to the setting and conditions required for the analyses given in this method.

9.8 Depending on specific program requirements, field replicates and field spikes of crude oil into samples may be required when this method is used to assess the precision and accuracy of the sampling and sample transporting techniques.

## 10.0 Calibration

10.1 Establish gas chromatographic/mass spectrometer operating conditions given in Table 1 of this appendix. Perform the GC/MS system hardware-tune as outlined by the manufacture. The gas chromatograph shall be calibrated using the internal standard technique.

NOTE: Because each GC is slightly different, it may be necessary to adjust the operating conditions (carrier gas flow rate and column temperature and temperature program) slightly until the retention times in Table 2 of this appendix are met.

TABLE 1—GAS CHROMATOGRAPH/MASS SPECTROMETER (GC/MS) OPERATION CONDITIONS

| Parameter | Setting |
|---|---|
| Injection pot | 280 °C |
| Transfer line | 280 °C |
| Detector | 280 °C |
| Initial Temperature | 50 °C |
| Initial Time | 5 minutes |
| Ramp | 50 to 300 °C @ 5 °C per minute |
| Final Temperature | 300 °C |
| Final Hold | 20 minutes or until all peaks have eluted |
| Carrier Gas | Helium |
| Flow rate | As required for standard operation |
| Split ratio | As required to meet performance criteria (~1:100) |
| Mass range | 35 to 600 amu |

TABLE 2—APPROXIMATE RETENTION TIME FOR COMPOUNDS

| Compound | Approximate retention time (minutes) |
|---|---|
| Toluene | 5.6 |
| Octane, n−$C_8$ | 7.2 |
| Ethylbenzene | 10.3 |
| 1,2,4-Trimethylbenzene | 16.0 |
| Decane, −$C_{10}$ | 16.1 |
| TCB (Internal Standard) | 21.3 |
| Dodecane, −$C_{12}$ | 22.9 |
| 1-Methylnaphthalene | 26.7 |
| 1-Tetradecene | 28.4 |
| Tetradecane, −$C_{14}$ | 28.7 |
| 1,3-Dimethylnaphthalene | 29.7 |

10.2 Internal standard calibration procedure—1,3,5-trichlorobenzene (TCB) has been shown to be free of interferences from diesel and crude oils and is a suitable internal standard.

10.3 The system performance test mix standards prepared in Section 7.2.4 of this appendix shall be used to establish retention times and establish qualitative detection limits.

10.3.1 Spike a 500-mL aliquot of the 1.25 mg/mL SPTM standard with 500 µL of the TCB internal standard solution.

10.3.2 Inject 1.0 µL of this spiked SPTM standard onto the GC/MS in order to demonstrate proper retention times. For the GC/MS used in the development of this method, the ten compounds in the mixture had typical retention times shown in Table 2 of this appendix. Extracted ion scans for m/z 91 and 105 showed a maximum abundance of 400,000.

10.3.3 Spike a 500-mL aliquot of the 0.125 mg/mL SPTM standard with 500 µL of the TCB internal standard solution.

10.3.4 Inject 1.0 μL of this spiked SPTM standard onto the GC/MS to monitor detectable levels. For the GC/MS used in the development of this test, all ten compounds showed a minimum peak height of three times signal to noise. Extracted ion scans for m/z 91 and 105 showed a maximum abundance of 40,000.

10.4 GC/MS crude oil/drilling fluid calibration—There are two methods of quantification: Total Area Integration ($C_8$–$C_{13}$) and EIP Area Integration using m/z's 91 and 105. The Total Area Integration method should be used as the primary technique for quantifying crude oil in NAFs. The EIP Area Integration method should be used as a confirmatory technique for NAFs. However, the EIP Area Integration method shall be used as the primary method for quantifying oil in enhanced mineral oil (EMO) based drilling fluid. Inject 1.0 μL of each of the four crude oil/drilling fluid calibration standards prepared in Section 7.2.5 of this appendix into the GC/MS. The internal standard should elute approximately 21–22 minutes after injection. For the GC/MS used in the development of this method, the internal standard peak was (35 to 40)% of full scale at an abundance of about 3.5e+07.

10.4.1 Total Area Integration Method—For each of the four calibration standards obtain the following: Using a straight baseline integration technique, obtain the total ion chromatogram (TIC) area from $C_8$ to $C_{13}$. Obtain the TIC area of the internal standard (TCB). Subtract the TCB area from the $C_8$–$C_{13}$ area to obtain the true $C_8$–$C_{13}$ area. Using the $C_8$–$C_{13}$ and TCB areas, and known internal standard concentration, generate a linear regression calibration using the internal standard method. The $r^2$ value for the linear regression curve shall be greater than or equal to 0.998. Some synthetic fluids might have peaks that elute in the window and would interfere with the analysis. In this case the integration window can be shifted to other areas of scan where there are no interfering peaks from the synthetic base fluid.

10.4.2 EIP Area Integration—For each of the four calibration standards generate Extracted Ion Profiles (EIPs) for m/z 91 and 105. Using straight baseline integration techniques, obtain the following EIP areas:

10.4.2.1 For m/z 91 integrate the area under the curve from approximately 9 minutes to 21–22 minutes, just prior to but not including the internal standard.

10.4.2.2 For m/z 105 integrate the area under the curve from approximately 10.5 minutes to 26.5 minutes.

10.4.2.3 Obtain the internal standard area from the TCB in each of the four calibration standards, using m/z 180.

10.4.2.4 Using the EIP areas for TCB, m/z 91 and m/z105, and the known concentration of internal standard, generate linear regression calibration curves for the target ions 91 and 105 using the internal standard method. The $r^2$ value for each of the EIP linear regression curves shall be greater than or equal to 0.998.

10.4.2.5 Some base fluids might produce a background level that would show up on the extracted ion profiles, but there should not be any real peaks (signal to noise ratio of 1:3) from the clean base fluids.

## 11.0 Procedure

11.1 Sample Preparation—

11.1.1 Mix the authentic field sample (drilling fluid) well. Transfer (weigh) a 30-g aliquot of the sample to a labeled centrifuge tube.

11.1.2 Centrifuge the aliquot for a minimum of 15 min at approximately 15,000 rpm, in order to obtain a solids free supernate.

11.1.3 Weigh 0.5 g of the supernate directly into a tared and appropriately labeled GC straight vial.

11.1.4 Spike the 0.5-g supernate with 500 μL of the 0.01g/mL 1,3,5-trichlorobenzene internal standard solution (*see* Section 7.2.3 of this appendix), cap with a Teflon lined crimp cap, and vortex for ca. 10 sec.

11.1.5 The sample is ready for GC/MS analysis.

11.2 Gas Chromatography.

Table 1 of this appendix summarizes the recommended operating conditions for the GC/MS. Retention times for the n-alkanes obtained under these conditions are given in Table 2 of this appendix. Other columns, chromatographic conditions, or detectors may be used if initial precision and accuracy requirements (Section 9.2 of this appendix) are met. The system shall be calibrated according to the procedures outlined in Section 10 of this appendix, and verified every 12 hours according to Section 11.6 of this appendix.

11.2.1 Samples shall be prepared (extracted) in a batch of no more than 20 samples. The batch shall consist of 20 authentic samples, 1 blank (Section 9.3 of this appendix), 1 matrix spike sample (9.4), and 1 duplicate field sample (9.5), and a prepared sample of the corresponding clean NAF used in the drilling process.

11.2.2 An analytical sequence shall be analyzed on the GC/MS where the 3 SPTM standards (Section 7.2.4 of this appendix) containing internal standard are analyzed first, followed by analysis of the four GC/MS crude oil/drilling fluid calibration standards (Section 7.2.5 of this appendix), analysis of the blank, matrix spike sample, the duplicate sample, the clean NAF sample, followed by the authentic samples.

11.2.3 Samples requiring dilution due to excessive signal shall be diluted using methylene chloride.

11.2.4 Inject 1.0 μL of the test sample or standard into the GC, using the conditions in Table 1 of this appendix.

11.2.5 Begin data collection and the temperature program at the time of injection.

11.2.6 Obtain a TIC and EIP fingerprint scans of the sample (Table 3 of this appendix).

11.2.7 If the area of the $C_8$ to $C_{13}$ peaks exceeds the calibration range of the system, dilute a fresh aliquot of the test sample weighing 0.50-g and re-analyze.

11.2.8 Determine the $C_8$ to $C_{13}$ TIC area, the TCB internal standard area, and the areas for the m/z 91 and 105 EIPs. These shall be used in the calculation of oil concentration in the samples (see Section 12 of this appendix).

TABLE 3—RECOMMENDED ION MASS NUMBERS

| Selected ion mass numbers | Corresponding aromatic compounds | Typical rentention time (minutes) |
|---|---|---|
| 91 | Methylbenzene | 6.0 |
| | Ethylbenzene | 10.3 |
| | 1,4-Dimethylbenzene | 10.9 |
| | 1,3-Dimethylbenzene | 10.9 |
| | 1,2-Dimethylbenzene | 11.9 |
| 105 | 1,3,5-Trimethylbenzene | 15.1 |
| | 1,2,4-Trimethylbenzene | 16.0 |
| | 1,2,3-Trimethylbenzene | 17.4 |
| 156 | 2,6-Dimethylnaphthalene | 28.9 |
| | 1,2-Dimethylnaphthalene | 29.4 |
| | 1,3-Dimethylnaphthalene | 29.7 |

11.2.9 Observe the presence of peaks in the EIPs that would confirm the presence of any target aromatic compounds. Using the EIP areas and EIP linear regression calibrations compare the abundance of the aromatic peaks, and if appropriate, determine approximate crude oil contamination in the sample for each of the target ions.

11.3 Qualitative Identification—See Section 17 of this method for schematic flowchart.

11.3.1 Qualitative identification shall be accomplished by comparison of the TIC and EIP area data from an authentic sample to the TIC and EIP area data from the calibration standards (*see* Section 10.4). Crude oil shall be identified by the presence of $C_{10}$ to $C_{13}$ n-alkanes and corresponding target aromatics.

11.3.2 Using the calibration data, establish the identity of the $C_8$ to $C_{13}$ peaks in the chromatogram of the sample. Using the calibration data, establish the identity of any target aromatics present on the extracted ion scans.

11.3.3 Crude oil is not present in a detectable amount in the sample if there are no target aromatics seen on the extracted ion scans. The experience of the analyst shall weigh heavily in the determination of the presence of peaks at a signal-to-noise ratio of 3 or greater.

11.3.4 If the chromatogram shows n-alkanes from $C_8$ to $C_{13}$ and target aromatics to be present, contamination by crude oil or diesel shall be suspected and quantitative analysis shall be determined. If there are no n-alkanes present that are not seen on the blank, and no target aromatics are seen, the sample can be considered to be free of contamination.

11.4 Quantitative Identification—

11.4.1 Determine the area of the peaks from $C_8$ to $C_{13}$ as outlined in the calibration section (10.4.1 of this appendix). If the area of the peaks for the sample is greater than that for the clean NAF (base fluid) use the crude oil/drilling fluid calibration TIC linear regression curve to determine approximate crude oil contamination.

11.4.2 Using the EIPs outlined in Section 10.4.2 of this appendix, determine the presence of any target aromatics. Using the integration techniques outlined in Section 10.4.2 of this appendix, obtain the EIP areas for m/z 91 and 105. Use the crude oil/drilling fluid calibration EIP linear regression curves to determine approximate crude oil contamination.

11.5 Complex Samples—

11.5.1 The most common interferences in the determination of crude oil can be from mineral oil, diesel oil, and proprietary additives in drilling fluids.

11.5.2 Mineral oil can typically be identified by its lower target aromatic content, and narrow range of strong peaks.

11.5.3 Diesel oil can typically be identified by low amounts of n-alkanes from $C_7$ to $C_9$, and the absence of n-alkanes greater than $C_{25}$.

11.5.4 Crude oils can usually be distinguished by the presence of high aromatics, increased intensities of $C_8$ to $C_{13}$ peaks, and/or the presence of higher hydrocarbons of $C_{25}$ and greater (which may be difficult to see in some synthetic fluids at low contamination levels).

11.5.4.1 Oil condensates from gas wells are low in molecular weight and will normally produce strong chromatographic peaks in the $C_8$–$C_{13}$ range. If a sample of the gas condensate crude oil from the formation is available, the oil can be distinguished from other potential sources of contamination by using it to prepare a calibration standard.

11.5.4.2 Asphaltene crude oils with API gravity <20 may not produce chromatographic peaks strong enough to show contamination at levels of the calibration. Extracted ion peaks should be easier to see than increased intensities for the C8 to C13 peaks. If a sample of asphaltene crude from the formation is available, a calibration standard shall be prepared.

11.6 System and Laboratory Performance—

11.6.1 At the beginning of each 8-hour shift during which analyses are performed,

GC crude oil/drilling fluid calibration and system performance test mixes shall be verified. For these tests, analysis of the medium-level calibration standard (1-% Reference Oil in IO Lab drilling fluid, and 1.25 mg/mL SPTM with internal standard) shall be used to verify all performance criteria. Adjustments and/or re-calibration (per Section 10 of this appendix) shall be performed until all performance criteria are met. Only after all performance criteria are met may samples and blanks be analyzed.

11.6.2 Inject 1.0 μL of the medium-level GC/MS crude oil/drilling fluid calibration standard into the GC instrument according to the procedures in Section 11.2 of this appendix. Verify that the linear regression curves for both TIC area and EIP areas are still valid using this continuing calibration standard.

11.6.3 After this analysis is complete, inject 1.0 μL of the 1.25 mg/mL SPTM (containing internal standard) into the GC instrument and verify the proper retention times are met (*see* Table 2 of this appendix).

11.6.4 Retention times—Retention time of the internal standard. The absolute retention time of the TCB internal standard shall be within the range 21.0 ±0.5 minutes. Relative retention times of the n-alkanes: The retention times of the n-alkanes relative to the TCB internal standard shall be similar to those given in Table 2 of this appendix.

11.6.17 Schematic Flowchart for Qualitative Identification

6.17 Schematic Flowchart for Qualitative Identification

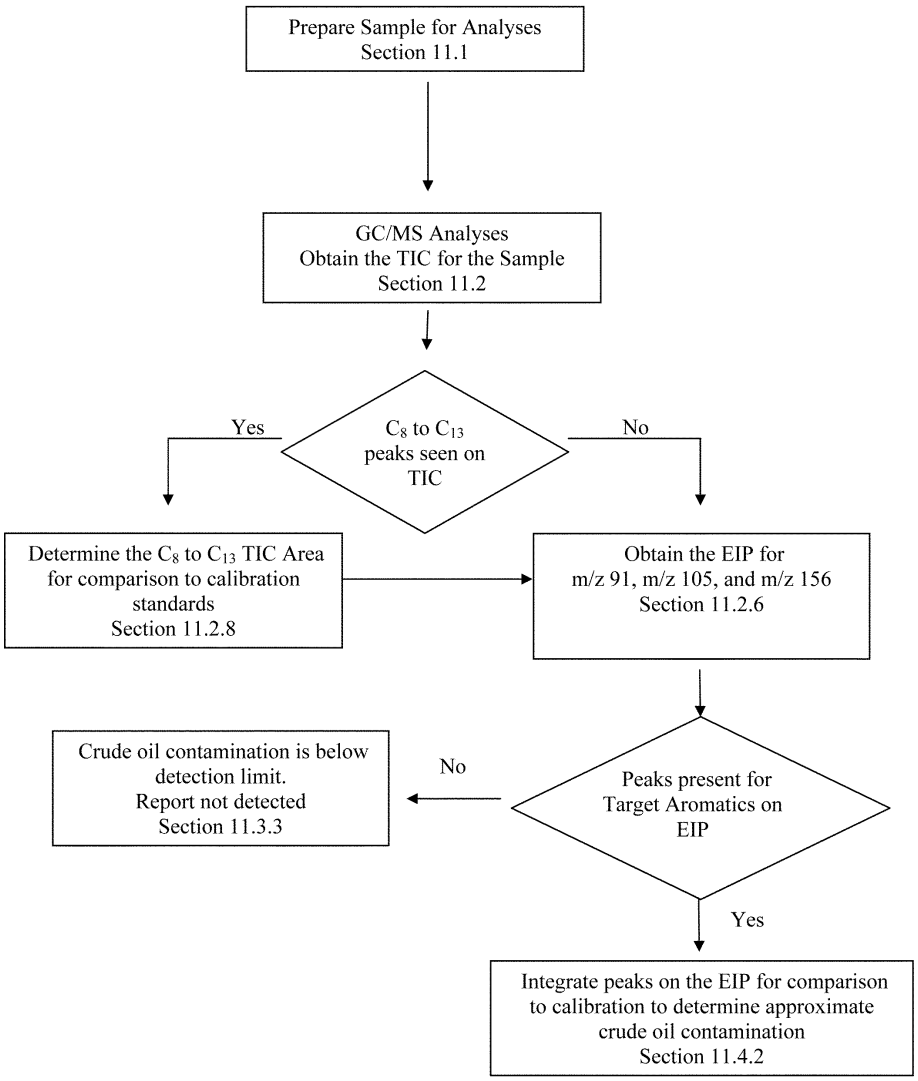


**Figure 1. Schematic Flowchart for Qualitative Identification**

12.0 CALCULATIONS

The concentration of oil in NAFs drilling fluids shall be computed relative to peak areas between $C_8$ and $C_{13}$ (using the Total Area Integration method) or total peak areas from extracted ion profiles (using the Extracted Ion Profile Method). In either case, there is a measurable amount of peak area, even in clean drilling fluid samples, due to spurious peaks and electrometer ''noise'' that contributes to the total signal measured using either of the quantification methods. In this procedure, a correction for this signal is applied, using the blank or clean sample correction technique described in American Society for Testing Materials (ASTM) Method D–3328–90, Comparison of Waterborne Oil by Gas Chromatography. In

this method, the ''oil equivalents'' measured in a blank sample by total area gas chromatography are subtracted from that determined for a field sample to arrive at the most accurate measure of oil residue in the authentic sample.

12.1 Total Area Integration Method

12.1.1 Using $C_8$ to $C_{13}$ TIC area, the TCB area in the clean NAF sample and the TIC linear regression curve, compute the oil equivalent concentration of the $C_8$ to $C_{13}$ retention time range in the clean NAF.

NOTE: The actual TIC area of the $C_8$ to $C_{13}$ is equal to the $C_8$ to $C_{13}$ area minus the area of the TCB.

12.1.2 Using the corresponding information for the authentic sample, compute the oil equivalent concentration of the $C_8$ to $C_{13}$ retention time range in the authentic sample.

12.1.3 Calculate the concentration (% oil) of oil in the sample by subtracting the oil equivalent concentration (% oil) found in the clean NAF from the oil equivalent concentration (% oil) found in the authentic sample.

12.2 EIP Area Integration Method

12.2.1 Using either m/z 91 or 105 EIP areas, the TCB area in the clean NAF sample, and the appropriate EIP linear regression curve, compute the oil equivalent concentration of the in the clean NAF.

12.2.2 Using the corresponding information for the authentic sample, compute its oil equivalent concentration.

12.2.3 Calculate the concentration (% oil) of oil in the sample by subtracting the oil equivalent concentration (% oil) found in the clean NAF from the oil equivalent concentration (% oil) found in the authentic sample.

### 13.0 METHOD PERFORMANCE

13.1 Specification in this method are adopted from EPA Method 1663, Differentiation of Diesel and Crude Oil by GC/FID (Reference 16.5).

13.2 Single laboratory method performance using an Internal Olefin (IO) drilling fluid fortified at 0.5% oil using a 35 API gravity oil was:

Precision and accuracy 94 ±4%
Accuracy interval—86.3% to 102%
Relative percent difference in duplicate analysis—6.2%

### 14.0 POLLUTION PREVENTION

14.1 The solvent used in this method poses little threat to the environment when recycled and managed properly.

### 15.0 WASTE MANAGEMENT

15.1 It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restriction, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required.

15.2 All authentic samples (drilling fluids) failing the RPE (fluorescence) test (indicated by the presence of fluorescence) shall be retained and classified as contaminated samples. Treatment and ultimate fate of these samples is not outlined in this SOP.

15.3 For further information on waste management, consult ''The Waste Management Manual for Laboratory Personnel'', and ''Less is Better: Laboratory Chemical Management for Waste Reduction'', both available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street NW, Washington, DC 20036.

### 16.0 REFERENCES

16.1 Carcinogens—''Working With Carcinogens.'' Department of Health, Education, and Welfare, Public Health Service, Centers for Disease Control (available through National Technical Information Systems, 5285 Port Royal Road, Springfield, VA 22161, document no. PB–277256): August 1977.

16.2 ''OSHA Safety and Health Standards, General Industry [29 CFR 1910], Revised.'' Occupational Safety and Health Administration, OSHA 2206. Washington, DC: January 1976.

16.3 ''Handbook of Analytical Quality Control in Water and Wastewater Laboratories.'' USEPA, EMSSL-CI, EPA–600/4–79–019. Cincinnati, OH: March 1979.

16.4 ''Method 1663, Differentiation of Diesel and Crude Oil by GC/FID, Methods for the Determination of Diesel, Mineral, and Crude Oils in Offshore Oil and Gas Industry Discharges, EPA 821–R–92–008, Office of Water Engineering and Analysis Division, Washington, DC: December 1992.

[66 FR 6901, Jan. 22, 2001, as amended at 77 FR 29843, May 18, 2012]

## APPENDIX 6 TO SUBPART A OF PART 435—REVERSE PHASE EXTRACTION (RPE) METHOD FOR DETECTION OF OIL CONTAMINATION IN NON-AQUEOUS DRILLING FLUIDS (NAF) (GC/MS) (EPA METHOD 1670)

### 1.0 SCOPE AND APPLICATION

1.1 This method is used for determination of crude or formation oil, or other petroleum oil contamination, in non-aqueous drilling fluids (NAFs).

1.2 This method is intended as a positive/negative test to determine a presence of crude oil in NAF prior to discharging drill cuttings from offshore production platforms.